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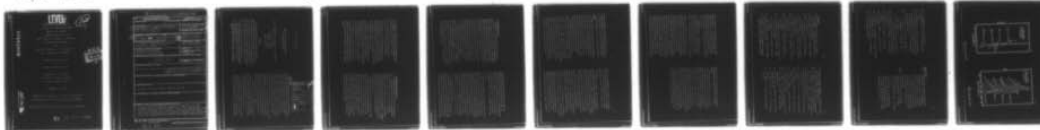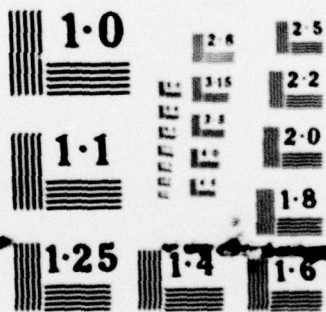
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Auger Spectra of Ammonia on Aluminum

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by

Charles T. Campbell, J. W. Rogers, Jr.,

R. L. Hance and J. M. White

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Auger Spectra of Ammonia on Aluminum and Oxidized Aluminum[a]

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Abstract

X-ray excited N(KVV) Auger spectra are reported for submonolayer amounts of ammonia adsorbed at 128K on clean and oxidized polycrystalline aluminum. The spectra were deconvoluted using an instrument function derived from the measured losses associated with the N(1s) photoionization region. The resulting spectra are compared with gas phase and condensed NH₃ spectra.

1. Introduction

Auger electron spectroscopy (AES) is widely used as a method for the elemental analysis of surfaces but the potential of this method for chemical state identification has only recently begun to be appreciated [1]. Experimentally, reports of the use of AES lineshapes to identify surface chemical species are scattered throughout the literature and include carbon [2-7], oxygen [8,9] and nitrogen [10] spectra. There are also reports of AES applied to free molecules [1, 11-17] and thick molecular films [1,18,19]. The unique chemical information that is contained in Auger spectra of molecular species derives mainly from the very localized character of the core hole. In a core-valence-valence Auger transition, the initial core hole probes the local valence electron distribution and the measured relative intensity and line shape are therefore sensitive to changes in this distribution. In order to exploit the potential of this method, careful studies of simple molecular systems must be available. This has been done using small organic molecules in the gas phase and in thick molecular films [1]. Similar data is available for ammonia [10,15-17].

From a surface science perspective, data for chemisorbed monolayer and submonolayer coverages is of considerable interest for at least two reasons: (1) to probe the intra-molecular bonding changes that occur on passing from either

the gas phase or a molecular film to a chemisorbed phase and (2) to determine the coupling of electronic states of the substrate with those of the adsorbate. Unfortunately instrument broadening, high background levels and characteristic loss processes tend to distort the intrinsic Auger line shape and a suitable response function must be employed for decon-voluting the data [20-22]. In the case of molecular films and chemisorbed layers this function should remove from the measured spectrum contributions due to the finite resolution of the analyzer, the energy width of the excitation source and non-Auger features (characteristic losses).

As part of a thorough electron spectroscopic study of small molecules on aluminum [23], we report here the deconvoluted x-ray excited Auger spectra (XAES) of monolayer coverages of NH_3 on clean and oxidized Al. A response function derived from the N(1s) region of the x-ray photo-electron spectrum (XPS), rather than that from the traditional electron backscatter spectrum, was employed. The resulting spectra are compared with known gas phase [19] and molecular film [18] data. To our knowledge these are the first reported deconvoluted AES spectra of monolayer coverages of molecular species.

2. Experimental and Deconvolution

The experimental procedure has been described previously [24]. Residual oxygen levels on the clean polycrystalline Al substrate were reduced to less than 5% of an equivalent monolayer with evidence indicating that this oxygen is distributed throughout the surface thickness sampled in these experiments (~ 50 Å) making the actual impurity level on the surface <1%. A dynamically pumped and calibrated multichannel array doser was employed. Spectra were generated using Mg (Kα) x-ray excitation and were recorded digitally. The double-pass cylindrical mirror analyzer was operated at a constant pass energy of 100 eV.

As measured, XAES data is generally distorted by a large and rapidly varying secondary electron background and by characteristic losses suffered by Auger electrons as they leave the solid. We have handled these distortions using a method which has been successfully applied to Li [25]. It uses an analytical approximation suggested by Sickafus [26] for secondary background removal and the van Cittert iterative deconvolution method [20,27] for removal of extrinsic energy losses and broadening due to finite analyzer resolution. Second-order polynomial least-squares smoothing [28] was applied uniformly to the deconvoluted data in an effort to reduce noise buildup [20,27].

3. Results and Discussion.

Loss spectra for ammonia-covered Al and oxided Al are shown in Fig. 1. Further proof of the identity of the adsorbed species described here can be found in ref. 36, which reports complimentary UPS and XPS data. A backscatter spectrum for 397 eV electrons interacting with an ammonia-saturated aluminum surface (128 K) is shown in Fig. 1(a). At this temperature, a multilayer cannot be formed [29] and the spectrum clearly shows bulk (15.9, 31.5 and 41.5 eV) and surface (9.75 eV) Al plasmons [30,31]. This spectrum is identical to that obtained for clean Al.

Figure 1(b) shows a spectrum under similar conditions except the Al surface was preoxided by exposure to 260 L of O_2 at room temperature to produce a 4-7 Å film of oxide [31]. The peaks at 7.2 eV and in the region between 15 and 22 eV can be explained in terms of an Al/Al_2O_3 interface plasmon [32] and surface and bulk plasmons in Al_2O_3 [33]. Both (a) and (b) illustrate that the presence of submonolayer coverages does not alter the loss features of the substrate.

The spectra of Fig. 1(c) and (d) show losses that occur behind the x-ray excited N(1s) core ionization. Figure 1(c) is for a submonolayer coverage comparable to (a) while (d) is for a multilayer of NH_3 condensed on Al at 108K. The no-loss peaks are the N(1s) photoelectron transitions for NH_3 (ads) (BE = 400.6 eV). To its right in (c) are the N(1s) transitions for dissociated NH_3 (BE = 396 eV) and the Mg $K\alpha_{3,4}$ satellite of the no-loss peak (BE = 391 eV).

In spectrum (d) there is no evidence for the dissociated ammonia feature while the x-ray satellite is clear. The only structure in the loss region of (d) is a broad featureless maximum near 22 eV. No substrate loss structure or losses characteristic of ammonia (6.5, 9 and 11 eV) are present [34]. It is interesting that (b) and (d) have similar lineshapes that appear to be characteristic of molecular crystals such as methanol [19].

The search for an appropriate instrument response function with which to deconvolute the XdS data prompted the investigation of the loss region associated with the N(1s) transition. Curve (c), after smoothing with a 9-point quadratic algorithm [28], was used because the losses experienced by a photoelectron escaping from a molecule adsorbed on top of the surface are more likely to be similar to those experienced by an Auger electron escaping under identical conditions, than to the losses experienced by a backscattered electron which is strongly coupled to substrate-related loss processes. This is particularly true in the present case due to the high intensity of plasmon losses in Al. One disadvantage of using the N(1s) transition is that the electron kinetic energy is much larger than for the Auger electron of interest.

The deconvoluted results for a 57 L exposure of NH_3 on clean and oxidised Al at 128 K are shown in Fig. 2 [29]. Also plotted for comparison, are the spectra for gas phase [17] and solid NH_3 [18]. The labels at the top of the figure refer to the two-hole final state of the Auger process. The spectra of the gas, solid and NH_3 (ads) on clean Al (curves a, b and d)

have been aligned with the presented spectrum (curve c) by shifting each spectrum to higher KE (by the amount indicated in the figure caption) so as to match the $1s^2$ peak positions.

The kinetic energies are referenced to the Fermi level of Al: BE[N(1s)] = 400.4 eV.

Theoretically, there are eleven possible transitions for NH₃ (gas) but several involve triplet final states and have low intensity [15]. Six well resolved bands appear in the gas phase spectrum (a). The orbitals involved in the transitions near 37] and 380 eV are valence orbitals with N-H and nitrogen lone-pair character respectively. Since UPS results [36] indicate that the nitrogen lone-pair ($3a_1$) participates in the surface bond, the $3a_1^2$ and $3a_1 1e$ transitions should be most affected in (b) and (c).

The solid NH₃ spectrum (d) exhibits five bands and a shoulder at ~385 eV. The $3a_1 1e$ and $3a_1^2$ peaks are not resolved. Larkins, et al. [18] attribute this to hydrogen bonding in the molecular crystal. They find transitions involving the $3a_1$ orbital are significantly broadened compared to the gas phase, from 2.2 to 7.0 eV in the case of the $3a_1^2$ transition. Jennison [18] has recently shown that hole-hole interactions in doubly ionized lone pair orbitals cause significant static relaxation effects. Condensed molecules which form hydrogen bonds exhibit large changes in the intensity of the transition derived from the doubly ionized lone pair orbital as compared to the gas phase [19].

Larkins et al. [18] suggest that the satellite, whose KE is slightly higher than the $3a_1 1e/3a_1^2$ bands, can be assigned to excitation of the N(1s) [2s₁] electron to an unfilled Rydberg state of the same symmetry, followed by a normal Auger process.

Unfortunately our results in Fig. 2 do not reflect the natural linewidths of the Auger lines, one desired result of deconvolution. This is because: 1) smoothing was necessary in the instrument response and the KATS spectra and 2) the N(1s) lines contain broadening due to the width of the excitation source which is not present in AES lines. The deconvolution here served mainly to remove the broad loss tail associated with electrons emitted from the NH₃(a) as shown in Fig. 1(c).

Spectra (b) and (c) show the deconvoluted N(KVV) transition for submonolayer coverages of NH₃ adsorbed on clean and oxidized Al. Curve (c) from Fig. 1, after additional smoothing, was used as the instrument response function in the deconvolution. In their raw form both spectra are broadened and show no pronounced features except the main associated with the $3a_1 1e$ and $1e^2$ transitions. The similarities between the spectral features of (b) and (c) with those of solid and gaseous NH₃ not only positively "fingerprint" the adsorbed species as molecular NH₃, but also justify the use of this response function for the deconvolution rather than that obtained by the electron backscattering method. To our knowledge, this is the first reported deconvolution of the Auger spectrum of a submonolayer coverage of an adsorbed

spectra. Spectrum (b), as compared to the others, shows a significant loss of intensity in the $3a_1^2$ region, a differential shift of the $3a_1$ le transition, and significant intensity in the satellite region. This ammonia is only weakly chemisorbed; thus, we ascribe most of these intensity shifts to final state relaxation effects due to the presence of the Al substrate.

The similarity between (c) and the spectrum of solid NH_3 (d) suggests that NH_3 is in a similar environment in the hydrogen bonded molecular crystal and on the oxidized surface. This is not surprising in view of the ionic nature of the oxidized Al surface and observed photoemission results [36]. Hydrogen bonding in the molecular crystal involves sharing of a covalently bonded, electropositive hydrogen atom with the lone-pair of a neighboring nitrogen atom. Oxidation of Al creates Lewis acid sites (Al^{6+}) in the surface region which, due to their small size and electropositive properties, should form a good substitute for a covalently bonded hydrogen in hydrogen bond formation. Comparing both (c) and (b) to (d), it is apparent that adsorption on the oxidized surface resembles solid NH_3 more than NH_3 adsorbed on clean Al. Both XPS and UPS data [36] indicate that more NH_3 is adsorbed on oxidized than clean Al surfaces. A greater concentration of NH_3 could tend to enhance the spectral features of (c) compared to (b). Oxidation of Al increases the surface area [37]; thus it cannot be determined from the present data whether the increased amount of NH_3 adsorbed on oxidized as compared to

clean Al, is due to a stronger interaction of Al_2O_3 with NH_3, or merely an increase in surface area following oxidation.

Further evidence supporting the conclusion that NH_3 bonded to oxidized Al is in an environment similar to that in a condensed NH_3 layer comes from the relative shifts in energy necessary for alignment of (b) and (d) with (c). Ammonia in a condensed multilayer is poorly screened by the substrate Fermi sea. As a result, the kinetic energies of all N(KVV) transitions are lower relative to those of a screened NH_3 molecule. The N(KVV) transitions shown in (b), for NH_3 bound to the clean metal are relaxed ~4.7 eV compared with solid NH_3. Likewise, localization of electron density from the Al Fermi sea into ionic Al-O bonds following oxidation, should render this surface less effective in screening holes created on adsorbed NH_3 molecules compared to clean Al. This is experimentally verified by comparison of (c) and (d) which are almost equivalently screened. In the totally unscreened case of gaseous NH_3 (a), the shift of all transitions is enormous (~10 eV) as expected.

References

[1] For an excellent review see R. R. Rye, J. E. Houston,
D. R. Jennison, T. E. Madey and P. H. Holloway, Ind. Eng.
Chem. Prod. Res. Devel. 18 (1979) 2.

[2] M. A. Chesters, B. J. Hopkins, A. R. Jones and R. Nathan,
Surf. Sci. 45 (1974) 740.

[3] (a) J. T. Grant and M. P. Hooker, J. Electron Spectros.
Relat. Phenom. 9 (1976) 93.

(b) M. P. Hooker and J. T. Grant, Surf. Sci. 55 (1976) 741.

[4] E. Umbach, J. C. Fuggle and D. Menzel, J. Electron Spectros.
Relat. Phenom. 10 (1977) 15.

[5] J. G. McCarty and R. J. Madix, J. Catal. 48 (1977) 422.

[6] D. W. Goodman, R. D. Kelley, T. E. Madey, and J. T. Yates, Jr.,
J. Catal. (in press).

[7] J. M. White and D. W. Goodman, Surface Sci. (in press).

[8] (a) T. Matsushima, D. B. Aley and J. M. White, Surf. Sci.
67 (1977) 89.

(b) T. Matsushima and J. M. White, Surf. Sci. 67 (1977) 122.

[9] (a) B. Carriere, J. P. Deville, G. Maire and P. Legare,
Surf. Sci. 58 (1976) 618.

(b) B. Carriere, P. Legare and G. Maire, J. Chim. Phys.
71 (1974) 355.

[10] T. Kawai, K. Kunimori, T. Kondow, T. Onishi and K. Tamaru,
Phys. Rev. Lett. 33 (1974) 533.

[11] L. Karlsson, L. O. Werme, T. Bergmark and K. Siegbahn,
J. Electron. Spectrosc. Relat. Phenom. 3 (1974) 181.

[12] R. Spohr, T. Bergmark, N. Magnusson, L. O. Werme, C. Nordling
and K. Siegbahn, Physica Scripta 2 (1970) 31.

[13] R. W. Shaw, Jr. and T. D. Thomas, Phys. Rev. A11 (1975) 1491.

[14] R. W. Moddeman, T. A. Carlson, M. O. Krause, B. P. Pullen,
W. E. Bull and G. K. Schweitzer, J. Chem. Phys. 55 (1971) 2317.

[15] R. W. Shaw, Jr., J. S. Jen and T. D. Thomas, J. Electron
Spectrosc. Relat. Phenom. 11 (1977) 91.

[16] R. Camilloni, G. Stefani and A. Giardini-Guidoni, Chem. Phys.
Lett. 50 (1977) 213.

[17] J. M. White, R. R. Rye and J. E. Houston, Chem. Phys. Lett.
46 (1977) 146.

[18] P. P. Larkins and A. Lubenfeld, J. Elect. Spectrosc. Relat.
Phenom. 15 (1979) 137.

[19] R. R. Rye, T. E. Madey, J. E. Houston, and P. H. Holloway,
J. Chem. Phys. 69 (1978) 1504.

[20] N. H. Madden and J. E. Houston, J. Appl. Phys. 47 (1976) 3071.

[21] J. E. Houston, J. Vac. Sci. Technol. 12 (1975) 255.

[22] J. E. Houston, G. Moore and M. G. Lagally, Solid State
Commun. 21 (1977) 879.

[23] J. V. Rogers, Jr., Ph.D. Dissertation, University of Texas
at Austin, August, 1979.

[24] J. V. Rogers, Jr. and J. M. White, J. Vac. Sci. Technol. 16
(1979) 485.

[25] N. H. Madden and J. E. Houston, Solid State Commun. 21
(1977) 1081.

[26] E. N. Sickafus, Rev. Sci. Inst. 42 (1971) 933.

[27] H. H. Madden and J. E. Houston, Adv. X-ray Analysis 19 (1976) 657.

[28] A. Savitzky and M. J. E. Golay, Anal. Chem. 36 (1964) 1627.

[29] On the basis of separate calibration experiments involving ammonia condensed at 106 K, we estimate an upper bound on the coverage in (a), (b) and (c) of 45% of a monolayer. Details are given in Ref. 23.

[30] C. J. Powell and J. B. Swan, Phys. Rev. 118 (1960) 640.

[31] (a) S. A. Flodström, R. Z. Bachrach, R. S. Bauer, J. C. McMenamin and S. B. M. Hagström, J. Vac. Sci. Technol. 14 (1977) 303.

(b) S. B. M. Hagström, R. Z. Bachrach, R. S. Bauer, and S. A. Flodström, Physica Scripta 16 (1977) 414.

[32] E. A. Stern and R. A. Ferrell, Phys. Rev. 120 (1960) 130.

[33] E. T. Arakawa and M. W. Williams, J. Phys. Chem. Solids 29 (1968) 735.

[34] A. Sherbele and E. N. Lassetre, J. Chem. Phys. 42 (1965) 395.

[35] M. T. Okland, R. Paegri, Jr. and R. Manne, Chem. Phys. Lett. 40 (1976) 185.

[36] J. W. Rogers, Jr., C. T. Campbell, R. L. Hance and J. M. White (to be published). Also ref. 23.

[37] M. W. Roberts and B. R. Wells, Surf. Sci. 15 (1969) 325.

[38] D. R. Jennison, submitted for publication.

Figure Captions

Figure 1. Electron energy loss spectra of NH_3 on clean and oxidized Al. a) electron backscatter spectrum of 397 eV electron on the Al surface saturated with NH_3 at 128 K. b) Same as (a) except the surface was preoxidized with 260 L O_2. c) Losses behind the N(1s) peak for the same conditions as (a). d) Losses behind N(1s) for a multilayer of NH_3 condensed on Al at 106K. BP = bulk plasmon, SP = surface plasmon, IP = interface plasmon.

Figure 2. IAES of the N(KVV) region, for adsorbed, condensed and gas phase NH_3. The spectra were arbitrarily shifted by an amount ΔE to align the $1e^2$ transitions with those of curve (C). a) NH_3 gas [17], $\Delta E = -9.1$ eV. b) Saturation NH_3 coverage on clean Al at 128 K, $\Delta E = -4.0$ eV. c) Saturation NH_3 coverage on oxidized (260 L O_2) Al at 128 K, $\Delta E = 0.0$ (reference). d) Condensed multilayer NH_3 [18], $\Delta E = +0.7$ eV.
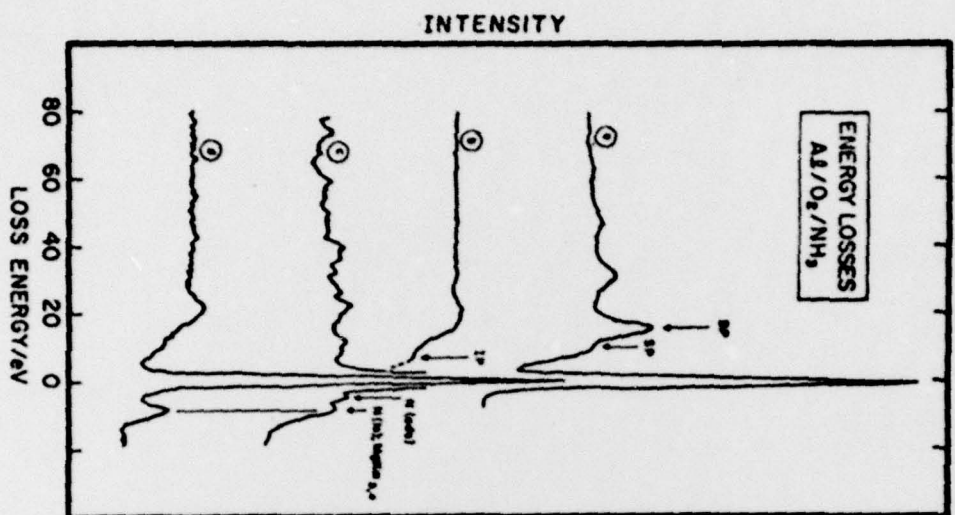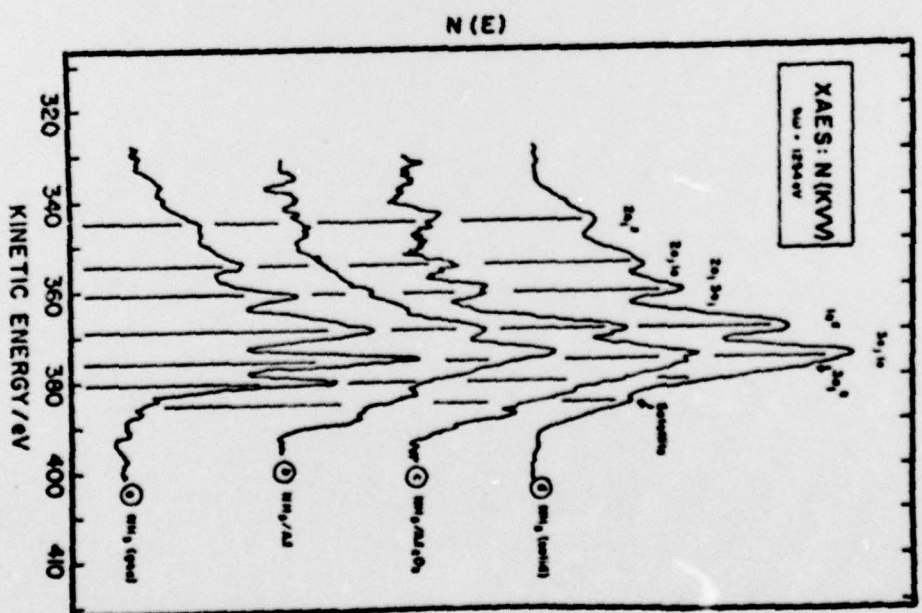
INTENSITY

ENERGY LOSSES
Ag/O₂/NH₃

LOSS ENERGY/eV

80   60   40   20   0

Fig. 1
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N(E)

XAES: N(KVV)
ℏω = 1254 eV

KINETIC ENERGY/eV

320   340   360   380   400   420   440

Fig. 2
Campbell, Capos, House, White

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